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IN SITU CONSERVATION BY CATHODIC PROTECTION OF CAST IRON FINDINGS IN MARINE ENVIRONMENT

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ABSTRACT

Nine cast iron cannons, dated between 17th and 18th century, were discovered in 2000 on the sea floor offshore the coast of the Marettimo Island (Sicily), scattered in an area of about 1200 square meters. The findings were left on the seabed, in the original place of their discovery, and a project for a marine archaeological park open to selected visitors was initiated by the Soprintendenza del Mare in collaboration with the Central Institute of Restoration. A comprehensive conservation plan was discussed among marine archeologists, conservators and materials engineers, aimed to identify efficient and non-invasive protection systems for the submerged cast iron objects. Cathodic protection was selected as the most interesting and promising conservation technique. Electrical protection of submerged steel components is a common practice for industrial or civil structures, that can be efficiently preserved circulating an external cathodic current on their surface using sacrificial anodes. In the case of components of artistic or historic relevance, particular care must be taken to guarantee the lowest impact on the object. Preliminary investigations concerning the materials and their conservation state (graphitization and corrosion potential), the position of the objects on the marine floor and the characteristics (temperature, pH, dissolved oxygen) of the environment were necessary. Zinc anodes were dimensioned and connected to the cannons by an original mounting structure.

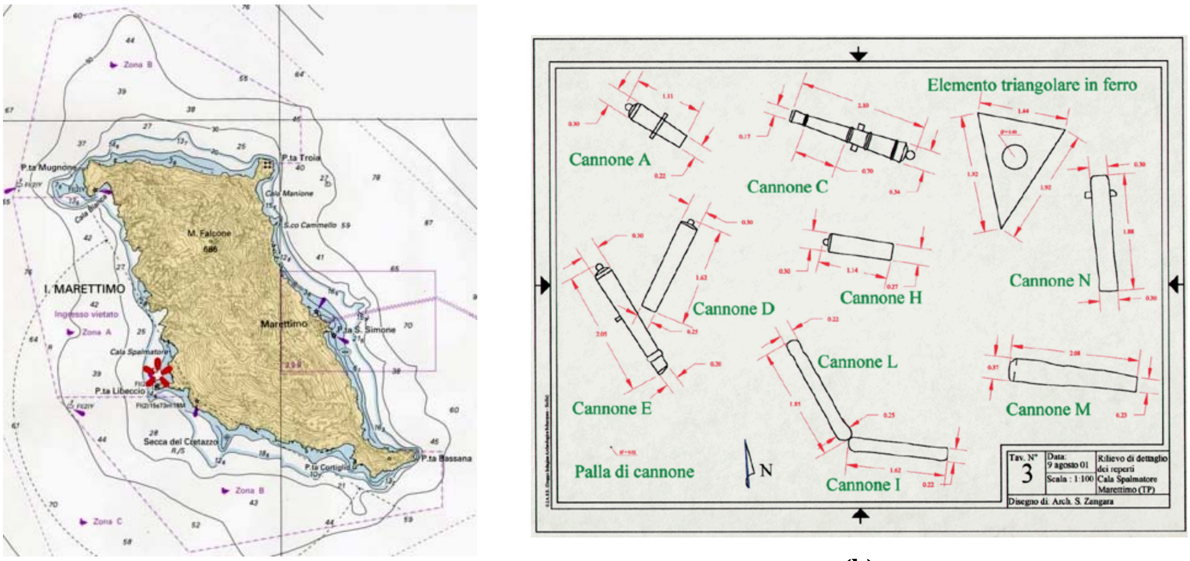
INTRODUCTION

Marettimo, the smallest of the Egadi Islands (Trapani, Sicily), is part of a Natural Reserve Park. A large variety of archaeological findings are lying on the seabed of the marine park: wrecks of carthaginian ships, wine amphorae, ancient bricks and tiles and other earthenware can be observed along prearranged sub-aqueous routes [1].

In 2000, a number of cast iron cannons shafts, dating between 17th and 18t^{h} century, was discovered on the sea floor offshore the Cala Spalmatore (see Fig. 1), dispersed as a consequence of the sinking of a Spanish ship. Nine cannons, of different size and shape, were found scattered in an area of about 1200 square meters at a depth of about 15 m.

The findings were left on the seabed, in the original place of their discovery, and a project for a marine archaeological park open to selected visitors was initiated by the Soprintendenza del Mare, in collaboration with ICR and Sapienza University of Rome.

The creation of Natural Marine Parks or Reserves and Protected Marine Areas also including areas of archaeological or historical interest, and the establishment of Underwater Archaeological Parks are proving to be effective instruments in safeguarding underwater cultural heritage [2-3], in full agreement with Unesco's recommendation of 2001 [4], proposing the exploitation, protection and *in situ* preservation of underwater archaeological heritage.



(a) **(b)**

Fig. 1: Location and survey of the archaeological site: nautical map of the island of Marettimo, with indication of the site, Cala Spalmatore (a); analytical survey of the 9 cannons (Soprintendenza del Mare, b).

The first step of the conservation work started on summer 2007. A comprehensive conservation plan was discussed among marine archeologists, conservators and materials engineers, aimed to identify efficient and non-invasive protection systems for the submerged cast iron objects. One of the cannons, whose surface had been cleaned back in 2000, was selected for the set up of the conservation plan, with the possibility of extending successful preservation procedures to the others in the next future.

Cathodic protection was selected as the most interesting and promising conservation technique. Electrical protection of submerged steel components is a common practice for industrial or civil structures, that can be efficiently preserved circulating an external cathodic current on their surface using sacrificial anodes. In the case of components of artistic or historic relevance, particular care must be taken to guarantee the lowest impact on the object.

In the late 1980s, I.D. MacLeod successfully experimented this method on many wrecks, some of them with metal structures, which had sunk as a result of naval combat during the Second World War, others, from the 18th and 19th centuries, with wooden hulls but containing iron cannons and anchors, such as the wrecks from Duart Point (the *Swan,* 1653 and the *Dartmouth,* 1690, Scotland) [5-15]. Periodic controls have confirmed the efficacy of this method and the stabilization of the corrosion processes [5]. For the wreck of the *San Pedro* (Florida Keys -USA), designated an archaeological marine reserve in 1989, the protection and *in situ* museum display was carried out covering the remaining of the wreck with ballast and protecting the iron anchor using a zinc bar as a sacrificial anode [16].

Details of the conservation plan designed for the Marettimo cannons are reported in the paper, together with very preliminary experimental results.

CORROSION OF LAMELLAR CAST IRON IN SEAWATER

Iron alloys in sea water can be corroded by either oxygen corrosion or, in anaerobic environment in the presence of particular depolarising bacterial species (the most common being *Sporovibrio Desulphuricans*), by so called sulphate-reducing bacteria corrosion. The corresponding mechanisms are illustrated below [17]:

Oxygen Corrosion

$Fe \rightarrow Fe^{2+} + 2e^-$	Anodic reaction
$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$	Cathodic reaction

Corrosion by Sulphate-Reducing Bacteria

$8H_2O \rightarrow 8H^+ + 8OH^-$	Hydrolysis
$4\ Fe \rightarrow 4Fe^{2+} + 8e^-$	Anodic reaction
$8H^+ + 8e^- \rightarrow 8H_{BIOL}$	Cathodic reaction
$8H_{BIOL} + Na_2SO_4 \rightarrow Na_2S + 4\ H_2O$	Sulphate reduction
$Fe^{2+} + Na_2S \rightarrow FeS\downarrow + 2Na+$	Insoluble products precipitation
$3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2\downarrow$	“ “ “

$$4Fe + Na_2SO_4 + 8H_2O \rightarrow 3FeS + 3Fe(OH)_2 + 2Na(OH)$$ Total reaction

A particular form of selective corrosion, known as graphitic corrosion, can occur when lamellar cast iron is exposed for long periods of time to sea water. While iron is converted to its corrosion products, some more corrosion-resistant micro-constituents of the alloy, particularly graphite, are retained and form a skeleton of graphite flakes stiffened and plugged by the carbonaceous debris resulting from the decomposition of the pearlite and by rust; this skeleton can retain sufficient strength to preserve the original contour of the component [17].

The graphitization depth is a direct function of the time of immersion of cast iron in seawater.

PRELIMINARY INVESTIGATIONS

Preliminary investigations concerning the environment, the materials and their conservation state, useful for a consistent cathodic protection project, were carried out during the first immersion in the archaeological site. The following geometrical and physical-chemical data were gathered:

Geometry of the cannon:
- length: 2.1 m
- external diameter of the breech: 0.34 m
- external diameter of the mouth: 0.17 m
- internal diameter of the mouth: 0.11 m

Environment:
- depth: 13.3 m
- pH: 8.1
- dissolved oxygen: 7.8 mg/l

The seabed in the site consists of areas of rocks, mainly colonized by algae and *Posidonia* alternate to limited extensions of sandy bottom. The alkaline value of pH, the high value of dissolved oxygen, the presence of *Posidonia* and the absence of lime lead to assume that the conditions for proliferation of sulphate-reduction bacteria are not met in the described environment.

A sample of the thick incrustation, formed since the cleaning operations dating summer 2000 and massively present over the entire surface of the cannon, was drawn for preliminary investigation of the condition of the artefact.

The biological colonization developed on the cannon surface was investigated by optical and scanning electron microscopy. Analyses showed that the surface was covered by various biological organisms, such as Rodhophyta (*Lithophyllum incrustans, Polysiphonia denudate, Jania rudens, Nemaliom helminthoides*) and Phaeophita (*Dictyota dicotomas, Dictyopetris membranacea, Padina pavonia*). Under the algae strata, the presence of *Pseudolithophyllum* was evidenced, sometimes with thalli colonized by the endolitic sponge *Cliona celata*. On the surface of *Pseudolithophyllum* were observed some Serpulids (*Spirorbis* with a limestone casing wrapped spiral) and bryozoans (*Lichenophora).*

An X-ray diffraction pattern of the pulverized material taken from the incrustation sample is shown in Fig. 3. The presence of calcium and magnesium carbonates and silicates was evidenced, together with iron corrosion products in the form of magnetite and goethite. No sulphur compound was detected, thus confirming the absence of corrosion phenomena induced by sulphate-reducing bacteria.

During the extraction of the sample, a surface graphitization layer, about 20 mm thick, was observed covering the metallic surface. This layer corresponds to the thickness of the cast iron artefact where the original metallic alloy has converted to a compact mass of iron corrosion products, kept together by the presence of graphite lamellae.

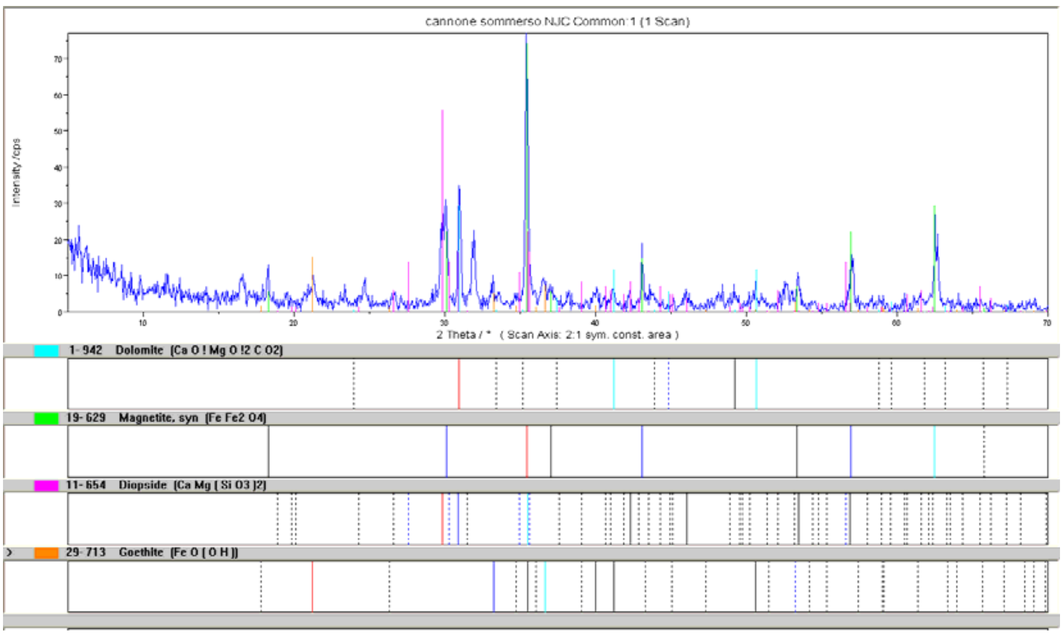


Fig. 3: X-ray diffraction pattern of pulverized material from a sample of surface incrustation: the position of standard lines relative to calcium and magnesium carbonates and silicates (dolomite and diopside) and to iron corrosion products (magnetite and goethite) are indicated under the pattern.

In order to assess the condition of the object in terms of corrosion processes active on its surface, measurements of surface potential were taken in different points over the external surface of the cannon, after drilling small holes across the concretion/graphitization layer.

Potential measurements were carried out using a Corrintec Rust Reader device (Corrintec Marine House, Chesterfield, UK), a self contained measuring probe designed for hand held diver operation, consisting of an Ag/AgCl reference electrode encased in a common water resistant shroud together with a digital voltmeter and connected to a replaceable hardened stainless steel tip enabling good electrical contact with the metallic surface (Fig. 4). Average values of potential measurements taken in correspondence with the breech and the mouth of the cannon, respectively, are indicated in Table 1. Corrosion potentials are reported as read by Rust Reader, referred to an Ag/AgCl reference electrode (-288 mV SHE), and after conversion for reference to a standard hydrogen electrode (SHE).

Open circuit potentials of - 500 mV Ag/AgCl indicate that the object is far from thermodynamically safe conditions (close to the immunity potential, normally assumed as about - 800 mV or – 900 mV in the presence of sulphate reducing bacteria [18]), and is therefore actively corroding. Any further inference about the actual corrosion rate corresponding to the mentioned values of potential should be considered arbitrary in the absence of additional details concerning the quality of the alloy and the characteristics of the environment, and in the absence of more abundant data, unavailable at this stage of the work.

	$E_{Ag/AgCl}$ (mV)	**E_{SHE} (mV)**
Cannon breech	- 500	- 212
Cannon mouth	- 497	- 209

Table I: Average corrosion potential values (mV) of the metallic surfaces, seven years after surface cleaning, before the application of CP: as read by Rust Reader, referred to an Ag/AgCl reference electrode, and as referred to a standard hydrogen electrode

Fig. 4: Corrosion potential measurement by Corrintec Rust Reader (Photo ICR)

CATHODIC PROTECTION

Cathodic protection (CP) is an electrochemical method used for preventing corrosion phenomena on a metallic surface. It can only be applied to metals exposed to conductive environments, and objects immersed in sea water can be particularly efficiently protected due to the very good properties of electrical conductivity of the medium.

The fundamental principle of the method is based on the possibility of modifying (reducing) the open circuit potential of an actively corroding metal by circulating a continuous current between an electrode, made of a less noble metallic material (sacrificial anode), and the object to be protected. The corrosion potential of the metal can be lowered down to the immunity potential, with a large current consumption and the risk of potentially dangerous side effects (such as the production of excessive amounts of atomic hydrogen), or can be alternatively reduced to values for which the corrosion rate can be considered acceptably low. As already mentioned, such limits are normally assumed for iron alloys as about - 800 mV vs Ag/AgCl, or – 900 mV in the presence of sulphate reducing bacteria.

For the cathodic protection of the examined cannon, zinc anodes from Seaguard Italanodi (Genova, Italy) were selected (Fig. 5a). Technical characteristics are reported in Fig. 5b.

(a)

Technical characteristics of Zn anodes:

Composition

Al	0.1-0.5%
Cd	0.025-0.07
Cu	0.005% max
Fe	0.005% max
Pb	0.006% max
Si	0.125% max
Zn	bal.

Potential: -1100 mV (Ag/AgCl)
Current capacity: 780 Ah/kg
Specific Consumption: 11.24 kg/A y

(b)

Fig. 5: Zinc anode (Seaguard Italanodi) used for cathodic protection: image (photo ICR, a) and technical characteristics (b)

Two anodes were electrically connected to the cannon and kept firmly in place by means of the purposely designed assembly illustrated in Fig 6, consisting of a stainless steel arch mounting two insulated pressure caps for stabilization and two metallic tips (insulated from the arch) for electrical connection with the cast-iron, under the graphitization layer.

A more specific dimensional design of the CP system (identification of the protection current, calculation of anodic output current and of the number of anodes for a given protection time) will be completed when further data will be made available during the next immersions, programmed for summer 2008. Measurement of corrosion potential after CP system installation are also in the course of acquisition.

Fig. 6: The assembly designed to be mounted on the breech of the cannon to install the cathodic protection system: the stainless steel structure, the insulated pressure caps and the metallic tips (insulated from the arch) for electrical connection with the cast-iron under the graphitization layer can be observed.

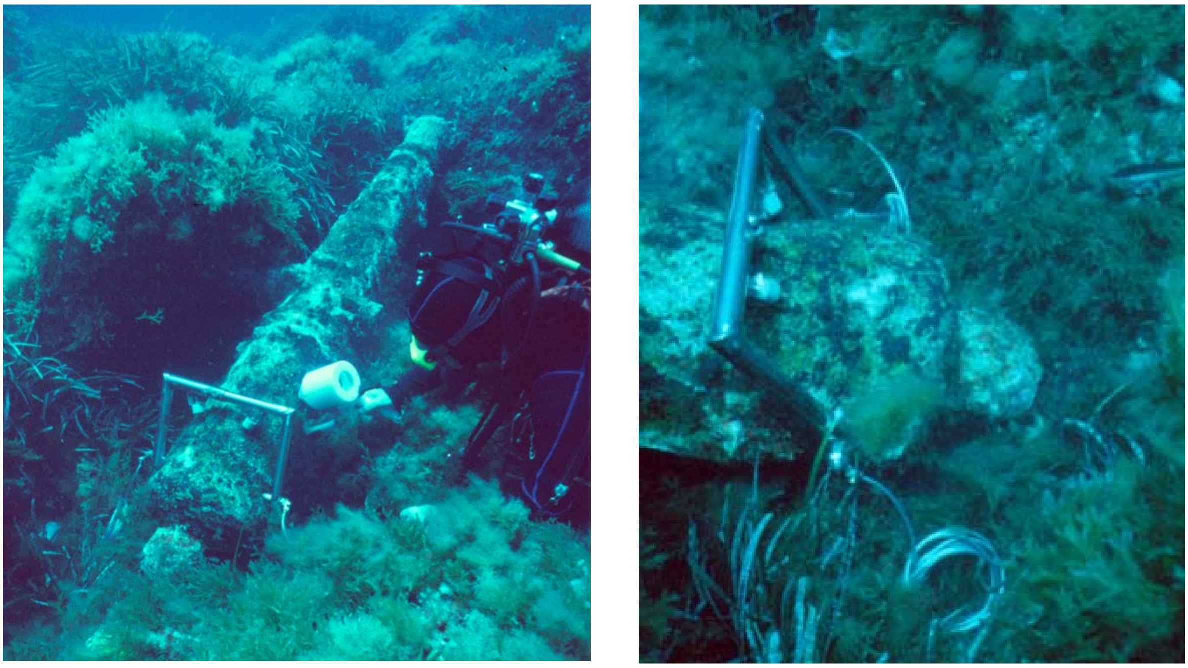


Fig. 7: Photographs of the cannon laying on the seabed after CP system installation: a) potential measurement by Corrintec; b) detail of the arch and the connected anode wires (photos ICR).

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